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TECHNICAL NOTE

ON THE THEORETICAL FOUNDATION OF THE  
ONE-ELECTRON APPROXIMATION

by

Lars T. Hedin

Quantum Chemistry Group  
For Research in Atomic, Molecular and Solid-State Theory  
Uppsala University, Uppsala, Sweden

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## SUMMARY

This paper can be divided into essentially two different parts. The first part contains a qualitative discussion of the one-electron approximation and a rough review of the Bohm-Pines, van Hove-Hugenholtz and Luttinger work. These works can be considered as representative of that part of current many-body literature which aims directly at the behavior of quasi-particles in normal many-fermion systems.

The second part of this paper tries to elaborate a specific method to handle quasi-particles. The method is formally similar to the usual Hartree-Fock scheme and it was chosen out of many possible approaches partly because the author has been actively working with it and partly because it is fairly simple and still illustrates the ideas and scope of present day many-body theories.

Some of the material given here has not been published earlier to the knowledge of the author. That goes for the iteration scheme developed to approximate the self-energy operator  $M$ , and also for the evaluation and discussion of the properties of the first non-trivial iteration step  $M^{(1)}$ , for some different physical systems, particularly for the hydrogen-like levels of alkali atoms. It is further shown that the Bohm-Pines treatment of single-particle properties corresponds to an "adiabatic" approximation of  $M^{(1)}$ . This approximation of  $M^{(1)}$  is however able to deal naturally also with the periodic lattice case.

## INTRODUCTION

The name one-electron approximation has almost become synonymous with the Hartree-Fock method (HF). Here we will, however, use that name for any scheme where a one-particle equation generates orbitals and orbital energies which are then used to describe the properties of the system.

When the first one-electron approximation was presented by Hartree<sup>1)</sup> in 1928, it was received with considerable reluctance. Already the same year Slater<sup>2)</sup> made a careful analysis of the errors that could be expected and showed that the amount of agreement obtained with experiment was by no means fortuitous. Despite that the Hartree equation was not generally accepted and used until a few years later when Slater<sup>3)</sup> and Fock<sup>4)</sup> independently showed that the Hartree equation augmented with an exchange term could be derived from the variational principle using a Slater determinant as trial function.

The HF method has had great success both in treating atoms, molecules and the band structure of solids. Concerning the band structure of solids, it is really not at all obvious that the HF method, considered to be founded on the variational principle, should give sensible results. The band structure describes the excitation energies which form a continuum. An excitation energy is obtained by subtracting one total energy from another. The variational principle tells us that each total energy is the best possible, which means it has a finite and quite large error. Thus the variational principle furnishes no direct reason why the HF method should give a sensible band structure. This kind of shortcoming of the variational principle also occurs, to a lesser extent, for the cohesive energies of solids and for the excitation energies of atoms and molecules. It is the purpose of this paper to try to explain, from a many-particle standpoint, why and when the HF equations give a reasonable description of excitation spectra and also to describe different attempts to improve the HF equation by a "correlation potential" or "polarization potential".

In the HF method the total wavefunction is described by one Slater determinant. A Slater determinant is really a very poor approximation to the true wave function and it can indeed be shown that the overlap integral between any Slater determinant and the true wave function tends to zero exponentially with the number of particles in any normal system. In a Slater determinant there is some correlation between particles of the same spin brought about by the Pauli principle (the Fermi hole), but correlation between

particles of opposite spin is totally missing.<sup>5)</sup> This effect can be studied for e.g. helium where very accurate wave functions have been calculated. If one keeps the position of one electron fixed and plots the wave function against the distance  $r$  between the two electrons there results the so called correlation hole or Coulomb hole, which for helium is a curve fairly well approximated by the expression  $C(1 + \frac{1}{2}r)$  up to  $r$  of the order of one atomic unit.

Though this correlation feature cannot be incorporated in any Slater determinant it can be brought into the HF equation itself by adding a correlation term. This cannot be justified if one looks upon the HF eq. as something providing orbitals for a complete  $N$  electron wave function but it is very reasonable if one takes the original intuitive standpoint Hartree had when first deriving the equations. Then one focuses attention on one specific electron and that electron should not see the average potential but there should be a correlation hole in the charge distribution of the other electrons. There are several treatments of such polarization effects. The simplest example is the case of an atom where one electron has an orbit lying outside the remaining ion. The polarization of the ion causes an extra term in the potential equal to  $-\frac{1}{2}a1/r^4$ , where  $a$  is the ion polarizability. Another famous example is the case of an electron moving in a highly excited state round a charged impurity in a semiconductor. The energy levels are then described quite accurately by a hydrogen-like formula with an effective mass and a dielectric constant. These two cases have been justified rigorously, the first by van Vleck and Whitelaw and independently Mayer and Mayer<sup>6)</sup> in 1933 and the second by Kohn<sup>7)</sup> in 1957. The single particle equations in these cases are really equations for quasiparticles or dressed particles, that is equations for a bare electron and a polarization cloud.

It was more difficult however to justify a polarization term in band calculations of crystals. Attempts were made by Callaway<sup>8)</sup> in 1957 to include polarization of the ion cores in alkali metals and by Wohlfarth<sup>9)</sup> in 1950 to use a screened Coulomb potential in the exchange term of an electron gas. It is only quite recently that one-electron equations with a polarization term for solids have obtained a proper interpretation.

### THE BOHM-PINES COLLECTIVE APPROACH

A large step forward towards the understanding of the behavior of electrons in a metal was made with the work by Bohm and Pines <sup>10)</sup> in 1953, which was extended and refined mainly by Pines. The basic idea was to treat first the collective behavior, i.e. the plasma vibrations of the electrons. The plasma vibrations are brought about by the long range of the coulomb force and are responsible for the long range correlation between the electrons. It is a high frequency phenomenon corresponding to energies of typically 10 to 20 eV, and it can be observed by measuring energy loss of fast electrons passing through thin metal foils.

As coordinates for the collective plasma vibrations Bohm and Pines used those Fourier components of the electron density for which  $k$  was smaller than some cut off value  $k_c$ . They also kept all electron coordinates and thus they had to introduce subsidiary conditions on the wave function to be justified in treating all considered coordinates independently. These subsidiary conditions have caused a good deal of trouble and form a weak point in the Bohm-Pines theory as also does the uncertainty in the choice of the cut off value  $k_c$ .

After writing the Hamiltonian in a form exhibiting the collective coordinates and adding terms containing collective momenta, the effect of which was nullified by the subsidiary conditions, Bohm and Pines performed a series of canonical transformations which brought the extended Hamiltonian on a form having a collective part, a quasi-particle part and supposedly weak interaction terms. The collective part had essentially an harmonic oscillator form and the quasi-particle part looked like the original Hamiltonian but with the coulomb potential replaced by a screened interaction of almost the Yukawa form,  $e^{-\lambda r}/r$ .

A reasonable first approximation for this Hamiltonian is a product of harmonic oscillator functions of the collective coordinates and a Slater determinant of plane waves. The collective part contains the long range correlation and the Slater determinant can be improved by a perturbation expansion in the short ranged interaction to include short range correlations. This perturbation expansion is convergent contrary to an expansion in the unscreened coulomb interaction,  $1/r$ .

In calculating the total energy the collective part is essential and brings about a very reasonable result, but in treating the single particle behavior the plasma part can be left out in the first approximation since the

large excitation energy of a "plasmon" makes it essentially frozen in, when only the low excitations close to the Fermi surface are considered. The quasi particle part in the Bohm Pines Hamiltonian has been successfully used in evaluating different single particle properties. A good review of the earlier calculations is given by Pines in Solid State Physics, vol. 1 (1955). More extended calculations have been made by Fletcher and Larsson <sup>11)</sup> (1958).

#### THE LINKED CLUSTER INFINITE PERTURBATION EXPANSION

The basic physical ideas behind the single particle behavior of electrons in solids is well described by the Bohm-Pines theory but more rigorous developments furnishing both exact formal results and quantitative estimates have utilized field theoretical methods. The first break through for infinite order perturbation theory treatment of many body systems came with the work by Brueckner <sup>12)</sup> in 1955. Ordinary Rayleigh-Schrödinger perturbation theory gives rise to terms of higher and higher powers in the number of particles  $N$ , but Brueckner showed explicitly for the lowest orders in the expansion that these unphysical terms cancel and he assumed that this mechanism worked for all orders. That this really is the case was shown by Goldstone <sup>13)</sup> who proved the so called linked cluster theorem. In the Brueckner-Goldstone expansion every term is represented by a linked cluster diagram giving a contribution at most proportional to  $N$ . Goldstone utilized methods and results from quantum field theory and his diagrams were those introduced by Feynman in 1949.

These results were almost immediately followed up by Hubbard <sup>14)</sup> who published two papers in 1957 on collective motions in terms of many-body perturbation theory. The first paper was purely formal and has become a corner stone in this field and the second contained a numerical calculation of the energy of an electron gas. The results agreed very well with those of Bohm and Pines.

### THE van HOVE-HUGENHOLTZ QUASI-PARTICLES

Parallel to the Brueckner-Goldstone-Hubbard work, van Hove and Hugenoltz<sup>15)</sup> during the years 1955 to 1958 developed their own technique to handle the perturbation theory of large quantum systems. They obtained results which in many respects went further than those of Goldstone and Hubbard, but since their technique was much more complicated it has not been so widely used. Their work centered on the properties of the low excitations in a Fermi gas, and the most important results are perhaps the following. Consider a low excited eigenstate of an Hamiltonian with no interparticle interactions. The statevector is a Slater determinant with  $N$  particles filling a Fermi sphere with radius  $k_F$  and one additional particle close to the Fermi surface. Switch on the interactions slowly (adiabatically). The resulting state is then an asymptotically stationary state of the full Hamiltonian with a decay time proportional to  $1/(k-k_F)^2$ . They also showed that the energy of the perturbed state when the extra particle is on the Fermi surface is equal to the ground state energy of the  $N$  particle system plus the average energy per particle.

The van Hove-Hugenoltz results apply only to a translationally invariant system, such as an electron gas, and the assumption that the infinite order perturbation expansion really converges has later been criticized by van Hove<sup>16)</sup> himself. Even if the series should diverge mathematically it could still provide a good asymptotic representation. The results must be considered as a large step towards the understanding of quasi-particles. Their results indicate that it is justified to use a model for the actual system with a single particle Hamiltonian whose eigenstates are in one to one correspondence with slowly decaying states of the true Hamiltonian. Approximate calculations of the decay time give a mean free path of the order of 100 000 Å at room temperature for an energy of the extra particle equal to  $kT$ <sup>17)</sup>. That is usually much longer than the mean free path due to phonon collisions and therefore negligible. The results are, however, incomplete in the respect that they apply only to the case with one particle outside a filled Fermi sphere and it remains to show that a model state corresponding to many excited particles has a true energy which is the sum of the corresponding quasi-particle energies. One has further to show that the adiabatic transforms of the low excited model states with all possible combinations of particles and holes (unfilled states inside the Fermi surface) really furnish all low excited true states.

### THE LUTTINGER THERMODYNAMIC APPROACH

A more general approach to the concept of a Fermi surface and properties connected with it has been made by Luttinger<sup>18)</sup> in a series of papers published in 1960 and 1961. His theory is applicable to non-zero temperatures. The partition function is represented by an infinite series expansion in a way first developed by Bloch and de Dominicis<sup>19)</sup> in 1958. The expansion is formally very similar to the Brueckner-Goldstone expansion, the Feynman propagators being modified to include temperature and a slightly larger class of diagrams to be considered. In the first two papers which were worked out together with Kohn and Ward it was shown that the extra diagrams in the statistical mechanical expansion, so called anomalous diagrams, in certain cases gave rise to non-zero contributions in the limit when  $T$  goes to zero. In these cases, which actually include the most interesting situations such as a periodic lattice, the Brueckner-Goldstone series has to be modified. During the detailed investigation necessary to establish this, several very interesting results appeared as by-products. Most of these were purely mathematical but for one thing they established that a certain class of quasi-stationary states of the interacting system in the translationally invariant case had a life-time proportional to  $1/(k-k_F)^2$ . These states are not the same as those considered by Hugenholtz and van Hove but are instead related to the Green functions or single particle propagators used by Martin and Schwinger and others.

In three papers Luttinger derived some very interesting results subject only to the restriction that the infinite order perturbation theory should be convergent or at least furnish a good asymptotic representation. He found that  $n_k$ , the mean occupation number for the plane wave state  $k$ , had a discontinuity on one or several surfaces in  $k$ -space which collection of surfaces he defined as the Fermi surface of the interacting system<sup>20)</sup>. In the translationally invariant case the Fermi surface is determined by the relation

$$\mu = \epsilon_k + K_k(\mu) \quad (1)$$

where  $\mu$  is the chemical potential,  $\epsilon_k$  is the energy in the non-interacting case,  $k^2/2$ , and  $K_k(E)$  is the real part of the so called self energy of the

quasi-particle,

$$K_k(E) \pm i J_k(E) \quad (2)$$

where we have plus sign when  $E < \mu$  and minus sign when  $E > \mu$ ,  $J_k(E) \geq 0$ ,  $J_k(\mu) = 0$ . The energy of the above-mentioned quasi-stationary state is

$$E_N + E_k \quad (3)$$

where  $E_N$  is the ground state energy of an  $N$ -particle system and  $E_k$  is determined by the equation

$$E_k = \epsilon_k + K_k(E_k) \quad (4)$$

$J_k(E_k)$  is the inverse of the lifetime of the state.

Luttinger also obtained exact results for the low temperature heat capacity, the spin paramagnetism, the compressibility and the characteristics of the de Haas-van Alphen oscillations. Most of the development is concerned with the translationally invariant situation but the main features of the theory in the band case are given and also an explicit expression for the heat capacity. The forms of these expressions are very similar to those in the non-interacting case. So is e.g. the heat capacity in the interactionless case proportional to the level density at the Fermi surface calculated from the orbital energies  $\epsilon_k$  whereas in Luttinger's expression the quasi-particle energies  $E_k$  appear and the integration is taken over the true Fermi surface. Luttinger also showed that the volume in  $k$ -space inside the Fermi surface is the same in the non-interacting and interacting cases. This means, of course, that the Fermi surface is unchanged in the translationally invariant case, since by symmetry it has to be spherical.

## THE GREEN FUNCTION FORMALISM

Besides the perturbation-theoretic treatment of many-body systems there is a large branch of research utilizing Green functions. The Schrödinger equation is then converted into a chain of coupled differential equations involving higher and higher orders of Green functions. The method used to handle this system is usually to insert a specific approximation for say the two-particle Green function and thus closing the system of equations. Green functions or particle propagators have long been used in field theory. Their statistical-mechanical versions were introduced by Matsubara <sup>21)</sup> in 1955 and the zero temperature forms were extensively treated with respect to their spectral properties by Galitskii and Migdal <sup>22)</sup> in 1958. The perhaps most well-known paper in this area is that by Martin and Schwinger <sup>23)</sup> in 1959.

We will not review any specific work on Green functions but instead make a development that borrows features from many different papers <sup>24)</sup> and leads straight to the derivation of a single particle equation where the orbitals and orbital energies have an exact interpretation with respect to the many body system. The orbital energies are actually identical to the quasi-particle energies used by Luttinger and the orbitals are simply related to the first order density matrix of the system. Such an equation was first derived by Pratt <sup>25)</sup> in 1960 starting from a theorem derived by Hugenholtz <sup>15)</sup> and by Bloch and Horowitz <sup>26)</sup>. Phillips <sup>27)</sup> derived a similar equation in 1961 from Hubbard's <sup>14)</sup> theory and gave a discussion of the order of magnitude of the different terms.

## SPECTRAL RESOLUTION OF THE ONE-PARTICLE GREEN FUNCTION

The one-particle Green function is defined as

$$G(x, x') = -i \langle N | T(\psi(x) \psi^\dagger(x')) | N \rangle \quad (5)$$

where  $x$  stands for three space coordinates and the spin and time coordinates.  $\psi(x)$  is the field operator in the Heisenberg representation and  $|N\rangle$  is the state vector for the ground state of an  $N$ -electron system.  $T$  is the time-ordering operator placing the operator with the latest time to the left and in-

serting a minus sign if the operators  $\psi$  and  $\psi^\dagger$  change places. For equal times  $G$  is defined as

$$G(\underline{x}, t; \underline{x}', t') = i \langle N | \psi^\dagger(\underline{x}', t) \psi(\underline{x}, t) | N \rangle = i \rho(\underline{x}, \underline{x}'), \quad (6)$$

where  $\underline{x}$  stands for space and spin coordinates and  $\rho(\underline{x}, \underline{x}')$  is the usual first order density matrix.  $G$  has a very direct physical interpretation which becomes clear if we take say  $t > t'$  and rewrite  $G$  slightly ( $E_N$  is the ground state energy of the  $N$ -particle system),

$$G(\underline{x}, t; \underline{x}', t') = -i \langle N | \psi(\underline{x}) e^{-iH\tau} \psi^\dagger(\underline{x}') | N \rangle = -i \langle \psi^\dagger(\underline{x}) N | e^{-iH\tau} \psi^\dagger(\underline{x}') N \rangle$$

$$H' = H - E_N, \quad \tau = t - t'. \quad (7)$$

Thus  $G$  gives the probability amplitude that a particle created at the point  $\underline{x}'$  at time  $t'$  reaches the point  $\underline{x}$  at time  $t$ . That statement is actually not quite true since the states involved are not normalized to unity but the relation anyhow makes it reasonable to call  $G$  a single particle propagator.

We will now consider the spectral resolution of  $G(\underline{x}, \underline{x}'; \tau)$ , where  $\tau = t - t'$ ,

$$G(\underline{x}, \underline{x}'; \tau) = -i \sum_k f_k(\underline{x}) f_k^*(\underline{x}') e^{-i\epsilon_k \tau} \quad \tau > 0$$

$$+ i \sum_\ell g_\ell(\underline{x}) g_\ell^*(\underline{x}') e^{-i\epsilon_\ell \tau} \quad \tau < 0 \quad (8)$$

where

$$\epsilon_k = E_{N+1, k} - E_N \quad \epsilon_\ell = E_N - E_{N-1, \ell}$$

$$f_k = \langle N | \psi(\underline{x}) | N+1, k \rangle \quad g_\ell = \langle N-1, \ell | \psi(\underline{x}) | N \rangle \quad (9)$$

In a HF approximation the state vectors are single Slater determinants and the  $g$ -functions then become the occupied orbitals, the  $f$ -functions the virtual orbitals and the  $\epsilon$ -values the corresponding orbital energies. In general there are an infinite number of  $g$ -functions. The  $f$ -functions and the  $g$ -functions are further not in general normalized to unity and each set has linear dependences between its functions. We now make a Fourier transform with respect to time,

$$G(\underline{x}, \underline{x}'; \epsilon) = \int_{-\infty}^{+\infty} G(\underline{x}, \underline{x}'; \tau) e^{i\epsilon\tau - \Delta|\tau|} d\tau = \sum_k \frac{f_k(\underline{x}) f_k^*(\underline{x}')}{\epsilon - \epsilon_k + i\Delta} + \sum_\ell \frac{g_\ell(\underline{x}) g_\ell^*(\underline{x}')}{\epsilon - \epsilon_\ell - i\Delta} \quad (10)$$

To have a unique definition for all  $\epsilon$  an infinitesimal positive convergence factor  $\Delta$  has been introduced. For a discrete spectrum  $G$  has simple poles at each of the "quasi-particle" energies  $\epsilon_k$  and  $\epsilon_\ell$ . For a continuous spectrum the sums are converted into integrals and the poles disappear.

### THE SELF-ENERGY OPERATOR $M$ AND THE QUASI-PARTICLES

It is convenient to introduce the self-energy operator  $M(x, x')$  which can be considered as defined by the relation (the Dyson equation),

$$G = G_0 + G_0 M G \quad (11)$$

where  $G_0$  is the Green function when there are no interparticle interactions and  $G_0 M G$  is a matrix product,  $x$  and  $x'$  being matrix indices. This relation becomes very simple when there is translational invariance since a Fourier transform with respect to space and time then factorizes the matrix product  $(G_0^{-1}(k, \epsilon) = \epsilon - \epsilon_k)$ , and all matrices are diagonal in spin),

$$G(k, \epsilon) = \frac{1}{\epsilon - \epsilon_k - M(k, \epsilon)} \quad , \quad M(k, \epsilon) = \begin{cases} K_k(\epsilon) + i J_k(\epsilon), \epsilon < \mu \\ K_k(\epsilon) - i J_k(\epsilon), \epsilon > \mu \end{cases} \quad (12)$$

$K_k$ ,  $J_k$ ,  $\epsilon_k$ , and  $\mu$  are the same quantities as used by Luttinger.  $M(k, \epsilon)$  can be analytically continued to complex values of  $\epsilon$ , the continuations being different, however, starting from the part of the real axis where  $\epsilon > \mu$  and the part where  $\epsilon < \mu$ . We now consider a value of  $\epsilon$  slightly larger than  $\mu$ .  $J_k(\epsilon)$  is then larger than zero but small. We may then assume that  $G(k, \epsilon)$  has a pole slightly under the real axis, say at  $\epsilon = \epsilon^*$ . By deforming the contour of integration for  $\epsilon$  in the expression

$$G(k, \tau) = \frac{1}{i\pi} \int_{-\infty}^{\infty} G(k, \epsilon) e^{-i\epsilon\tau} d\epsilon, \quad \tau > 0 \quad (13)$$

to run as

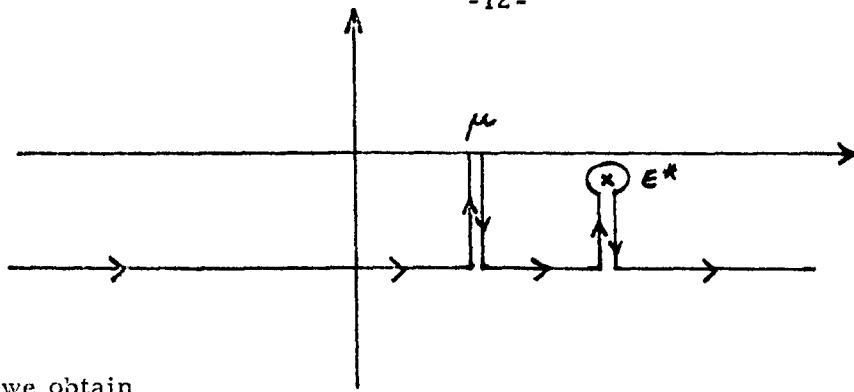


Fig. 1

we obtain

$$G(\underline{k}, \tau) = -i e^{-i \epsilon^* \tau} + \dots = -i e^{-i(\epsilon_k + K_k) \tau - J_k(\tau)} + \dots \quad (14)$$

The  $+ \dots$  comes from the contribution for  $\epsilon = \mu + i \epsilon_2$  since  $G(\underline{k}, \epsilon)$  is different in the upward and downward paths, these paths belonging to different analytical continuations. There could also possibly be more poles than the one at  $\epsilon^*$  and the contour has then to be deformed correspondingly. Assuming the  $+ \dots$  terms to be small<sup>22)</sup> we find that  $G(\underline{k}, \tau)$  describes a quasi-particle with energy  $\epsilon_k + K_k - i J_k$ . We can also study  $G$  from its spectral resolution, eq. (8). An approximately exponential dependence of  $\tau$  will result if the  $k$ :th Fourier component of the  $ff^*$ -products is essentially different from zero only within a narrow energy region for the  $\epsilon_k$ . The center of this region is then  $\epsilon_k + K_k$  and its spread  $J_k$ .

#### THE EQUATION FOR $G$ AND FOR THE AMPLITUDES

We now return to the case with no translational invariance. After Fourier transforming the Dyson equation, (11), with respect to time, where we still have translational invariance, and utilizing the relation  $G_0^{-1}(\epsilon) = \epsilon - h$ , where  $h$  is the relevant single particle operator, we obtain

$$(\epsilon - h - M(\underline{z})) G(\epsilon) = 1 \quad (15)$$

where the matrix indices  $\underline{x}$  and  $\underline{x}'$  are suppressed. Inserting the spectral resolution for  $G(\epsilon)$  and the identity

$$\sum_k f_k(\underline{x}) f_k^*(\underline{x}') + \sum_i g_i(\underline{x}) g_i^*(\underline{x}') = \delta(\underline{x} - \underline{x}') \quad (16)$$

which is trivially obtained from the anticommutation relation of  $\psi$  and  $\psi^\dagger$

we obtain

$$(\epsilon - h - M(\epsilon)) \left( \sum_k \frac{f_k f_k^*}{\epsilon - \epsilon_k + i\delta} + \sum_l \frac{g_l g_l^*}{\epsilon - \epsilon_l - i\delta} \right) = \sum_k f_k f_k^* + \sum_l g_l g_l^* \quad (17)$$

Now let  $\epsilon$  approach  $\epsilon_k$  and assume that those  $f_k$  for which the  $\epsilon_k$  are equal, are linearly independent. We then have

$$(\epsilon_k - h - M(\epsilon_k)) f_k = 0. \quad (18)$$

This is the single particle equation we set out to derive. The assumption made about linear independence of the  $f_k$  is really very weak as can be checked by considering explicit examples. The  $f_k$  for different  $\epsilon_k$  are on the other hand by no means in general linearly independent. A similar equation is of course also obtained for the  $g_k$ . The equation is valid when  $E_{N+1}$ ,  $k$  is a discrete energy level. It is also valid when  $E_{N+1}$  is continuous if  $E$  becomes discrete when we consider only a specific symmetry of the  $f$  as in the case of an extra particle in a semi-conductor. The first non-trivial approximation to this equation in case of a semiconductor was derived by Pratt<sup>25)</sup> (1960). The equation in its general form was suggested by Hedin and Lundqvist<sup>28)</sup> (1960) but the amplitudes  $g_k$  were there erroneously identified with the Löwdin<sup>29)</sup> natural spin-orbitals.

For a discrete spectrum  $G(\epsilon)$  and  $G_0(\epsilon)$  are Hermitian and thus  $M(\epsilon) = G_0^{-1}(\epsilon) - G^{-1}(\epsilon)$  is Hermitian, but for a continuous spectrum  $M(\epsilon)$  is not Hermitian in general. We can then consider the equation

$$(\epsilon - h - M(\epsilon)) \phi = 0, \quad (19)$$

and try to interpret it. When the  $M$ -operator is non-Hermitian, the eigenvalues  $\epsilon$  in general become complex. In analogy with the analysis made for  $G(\tau)$  in the translationally invariant case one might expect that  $\phi$  corresponds to a wave-packet of functions  $f_k$  and the real part of  $\epsilon$  to their mean energy. In case of one extra electron in an insulator,  $M$  remains Hermitian for a certain range of  $\epsilon$ -values. This case has been treated extensively by Kohn and Ambegaokar<sup>30)</sup> from a more general point of view than the above equation.

### APPROXIMATIONS TO THE M-OPERATOR

To make the equation useful we now have to obtain approximations to the M-operator. One method is to make a perturbation expansion for  $M$ , which can be represented by a well known set of diagrams. We can also utilize the Martin and Schwinger<sup>23)</sup> method with functional derivatives, and thus circumvent the usual convergence difficulties. It is then possible to obtain an expansion in higher and higher orders of correlation functions

$$\langle T(\rho'(1) \rho'(2)) \rangle, \langle T(\rho'(1) \rho'(2) \rho'(3)) \rangle, \dots \quad (20)$$

where

$$\rho'(1) = \psi^+(1) \psi(1) - \langle \psi^+(1) \psi(1) \rangle. \quad (21)$$

Each order is obtained by an iteration procedure and the expansion could reasonably be expected to have much better convergence properties than the usual one in  $e^2$ . The details of the derivation are evaluated in an appendix since the possibility of using an iteration scheme is not pointed out earlier in the literature to the knowledge of the author.

The first approximation is Hartree-like

$$(\epsilon_k - h(\underline{x}) - V(\underline{x})) f_k(\underline{x}) = 0, \quad (22)$$

where

$$V(\underline{x}) = \int v(\underline{x}, \underline{x}') \langle \rho(\underline{x}') \rangle d\underline{x}', \quad v(\underline{x}, \underline{x}') = \frac{e^2}{|\underline{x} - \underline{x}'|},$$

and  $\langle \rho(\underline{x}) \rangle$  is the true density of the  $N$  electron system. The next iteration is,

$$(\epsilon_k - h(\underline{x}) - V(\underline{x})) f_k(\underline{x}) - \int M^{(1)}(\underline{x}, \underline{x}'; \epsilon_k) f_k(\underline{x}') d\underline{x}' = 0, \quad (24)$$

where

$$M^{(1)}(\underline{x}, \underline{x}'; \epsilon) = \frac{i}{2\pi} \int_{-\infty}^{\infty} G(\underline{x}, \underline{x}'; \epsilon - \epsilon') \mathcal{V}(\underline{x}, \underline{x}'; \epsilon') d\epsilon', \quad (25)$$

and  $\mathcal{V}(\underline{x}, \underline{x}')$  is a screened potential first introduced by Hubbard,

$$\mathcal{V}(\underline{x}, \underline{x}') = v(\underline{x}, \underline{x}') - i \int v(\underline{x}, \underline{y}) \langle T(\rho'(\underline{y}) \rho'(\underline{y}')) \rangle v(\underline{y}, \underline{x}') d\underline{y} d\underline{y}'$$

$$v(\underline{x}, \underline{x}') = v(\underline{x}, \underline{x}') \delta(t - t')$$

If the correlation term in  $\mathcal{V}$  is neglected we are back to a HF-like approximation. The correlation term is, however, quite tractable since it is re-

lated in a simple way to the linear response function of the system, which in turn can be approximately evaluated from a time-dependent Hartree or HF treatment.  $G$  could be approximated with the solution for the Hartree or HF-like equation. The next term is much more complicated and hard to deal with, though Hubbard has tried to include it in a qualitative way in his treatment of the electron gas. Hubbard <sup>14)</sup> treated  $M^{(1)}$  by numerical methods in the above mentioned approximation (time dependent Hartree and  $G = G_0$ ) whereas Gell-Mann and Brueckner <sup>31)</sup> (1957) and DuBois <sup>32)</sup> (1959) made an expansion in  $r_s$ , the interparticle distance. This expansion is only valid at most up to  $r_s = 2$ , but one could hope that the complete  $M^{(1)}$  term should give a reasonable approximation also in the metallic density region ( $r_s = 2-5$ ). We will call  $M^{(1)}$  the polarization approximation for  $M$ , for reasons which will become clear in the next section.

#### DISCUSSION OF THE POLARIZATION APPROXIMATION FOR $M$

The formal properties of the polarization approximation for  $M$ , eq. (25), such as its spectral resolution and its relation to the linear response function are discussed in an appendix. In this section we will utilize these results in a discussion of how the approximation works for some simple physical systems and how it is related to approximations developed by other authors.

Let us first consider the simple situation of an electron moving well outside a closed shell ion. The energy levels are then to a first approximation hydrogen-like. Exchange effects have little influence but the polarization of the ion by the outer electron gives a small shift of the hydrogen-like energy levels which has been observed to a fair accuracy <sup>6, 33)</sup>.

A simple and reasonably accurate way to calculate this shift is furnished by an "adiabatic" approximation <sup>34)</sup>. The outer electron is then considered as a fixed point charge which polarizes the ion. The induced charge density  $\rho(\underline{x})$  gives rise to an extra potential  $\phi(\underline{x})$ , which acts back on the outer electron,

$$\phi(\underline{x}) = \frac{1}{2} \int \nabla(\underline{x}, \underline{x}') \rho(\underline{x}') d\underline{x}' \quad (27)$$

The factor  $\frac{1}{2}$  arises since  $-\text{grad } \phi(\underline{x})$  has to give the force on the outer elec-

tron and the gradient acts on both  $v$  and  $\rho(\underline{x}')$ , the latter containing  $\underline{x}$  implicitly. Calculating the induced charge by linear response we have from eq. (B16)

$$\phi(\underline{x}) = R(\underline{x}, \underline{x}; 0) = F(\underline{x}, \underline{x}; 0), \quad (28)$$

where

$$F(\underline{x}, \underline{x}'; 0) = - \sum_s' \frac{P_s(\underline{x}) P_s^*(\underline{x}')}{{E}_{N,s} - {E}_{N,0}} \quad (29)$$

$$P_s(\underline{x}) = \int v(\underline{x}, \underline{x}') \langle N | \rho(\underline{x}') | N, s \rangle d\underline{x}'.$$

An equivalent result can be obtained by a quite rigorous treatment.

Since  $\phi(\underline{x})$  is a small perturbation it is sufficient to consider its expectation value with respect to the outer electron orbital. Using the assumption that this orbital is well outside the ion and observing that the expression

$$\sum_s' \frac{\langle N | \rho(\underline{x}) | N, s \rangle \langle N, s | \rho(\underline{x}') | N \rangle}{{E}_{N,s} - {E}_{N,0}} \quad (30)$$

is essentially different from zero only when  $\underline{x}$  and  $\underline{x}'$  are more or less inside the ion (the expression (30) is the kernel in the linear response function and we do not expect much induced charge outside the ion), we can obtain a good approximation of  $\phi(\underline{x})$  by making a multipole expansion of the coulomb potentials. The constant terms vanish and if we keep only the dipole terms we have

$$F(\underline{x}, \underline{x}'; 0) = - \sum_s' \frac{(\underline{x} \cdot \underline{R}_s)(\underline{x}' \cdot \underline{R}_s^*)}{{E}_{N,s} - {E}_{N,0}} \frac{1}{|\underline{x}|^3} \frac{1}{|\underline{x}'|^3} = -\frac{1}{2} \frac{\underline{x} \cdot \underline{x}'}{|\underline{x}|^3 |\underline{x}'|^3} \sum_s' \frac{2}{3} \frac{\underline{R}_s \cdot \underline{R}_s^*}{{E}_{N,s} - {E}_{N,0}}$$

$$\underline{R}_s = \langle N, 0 | \sum_{i=1}^N \underline{x}_i | N, s \rangle \quad (31)$$

and thus

$$\phi(\underline{x}) = -\frac{1}{2} \frac{1}{|\underline{x}|^4} \alpha \quad (32)$$

where  $\alpha$  is the static polarizability of the ion. This result can also be obtained from a very simple argument as shown by Born and Heisenberg<sup>35)</sup> in 1924.

We now want to show how the polarization approximation for  $M$  can reproduce eq. (28). From the appendix, eq. (B4), we find that  $M^{(1)}$  is equal to a HF-like exchange term, which we neglect in this case, plus a polarization potential  $V_p$ . From eq. (B10) we have,

$$(f_k | V_p(\underline{r}_k; \epsilon_k) | f_k) = (f_k | \sum_{k'} f_{k'} f_{k'}^* F(\epsilon_k - \epsilon_{k'}) | f_k) \quad (33)$$

where  $f_k$  is the outer orbital we are considering, and terms with  $\epsilon_k < \mu$  have been neglected since they contain ion orbitals and thus are small where  $f_k$  is appreciable. Since the ion has a closed shell structure we can assume that the ion excitation energies are much larger than the differences  $\epsilon_k - \epsilon_{k'}$  for those  $k'$  where  $f_{k'}$  and  $f_k$  have significant overlap. Thus we approximate

$$\begin{aligned} (f_k | V_p(\epsilon_k) | f_k) &= (f_k | \sum_{k'} f_{k'} f_{k'}^* F(0) | f_k) = \\ &= \int f_k^*(\underline{x}) \delta(\underline{x} - \underline{x}') F(\underline{x}, \underline{x}'; 0) f_k(\underline{x}') d\underline{x} d\underline{x}' \end{aligned} \quad (34)$$

and have by that obtained the same approximation as the "adiabatic" one.

Another method to approximate the polarization approximation is obtained by making an assumption about the time behavior of  $G$  and  $\mathcal{V}$ .

$\mathcal{V}(\tau)$  without the polarization part is simply  $v(\tau)$  which contains a  $\delta$ -function in  $\tau$ . We now assume that polarization does not broaden this  $\delta$ -function peak too much, so that the time variation of  $G(\tau)$  within the peak still can be neglected except for the discontinuity of  $G(\tau)$  at  $\tau = 0$ . Using the HF-approximation for  $G$  we have

$$G(\underline{x}, \underline{x}'; \tau) = -i e^{-i h(\underline{x}) \tau} \left[ \theta(\tau) \sum_{k}^{unocc} u_k(\underline{x}) u_k^*(\underline{x}') - \theta(-\tau) \sum_{k}^{occ} u_k(\underline{x}) u_k^*(\underline{x}') \right] \quad (35)$$

where  $\theta(\tau) = \begin{cases} 1 & \tau > 0 \\ 0 & \tau < 0 \end{cases}$

Our assumption about the time dependences amounts to putting  $e^{-i h \tau} = 1$ . Using the identity

$$\sum_{k}^{unocc} u_k(\underline{x}) u_k^*(\underline{x}') + \sum_{k}^{occ} u_k(\underline{x}) u_k^*(\underline{x}') = \delta(\underline{x} - \underline{x}'), \quad (36)$$

we then have

$$G(\underline{x}, \underline{x}'; \tau) = -i \left( \theta(\tau) \delta(\underline{x} - \underline{x}') - \sum_{k}^{occ} u_k(\underline{x}) u_k^*(\underline{x}') \right). \quad (37)$$

From (A25) and (37) we obtain

$$\begin{aligned} M^{(1)}(\underline{x}, \underline{x}'; \tau) &= i G(\underline{x}, \underline{x}'; \tau) \mathcal{V}(\underline{x}, \underline{x}'; \tau) = \\ &= \theta(\tau) \delta(\underline{x} - \underline{x}') \left( \mathcal{V}(\underline{x}, \underline{x}'; \tau) - v(\underline{x}, \underline{x}'; \tau) \right) - \sum_{k}^{occ} u_k(\underline{x}) u_k^*(\underline{x}') \mathcal{V}(\underline{x}, \underline{x}'; \tau) \end{aligned} \quad (38)$$

Since  $v(\tau^+) \theta(\tau) = 0$  we are allowed to put an extra  $v$  into the first term of the last member of (38), thus emphasizing that this term only contains the polarization part of  $\mathcal{V}$ . Performing a Fourier transform with respect to time we have, compare with (B6),

$$M^{(1)}(x, x'; \epsilon) = \delta(x - x') F(x, x'; \epsilon) - \sum_{\mathbf{k}}^{\text{occ}} u_{\mathbf{k}}(x) u_{\mathbf{k}}^*(x') \mathcal{V}(x, x'; \epsilon). \quad (39)$$

$M(x, x'; 0)$  thus gives the "adiabatic" approximation with one modification, namely we have a screened potential  $\mathcal{V}$  instead of  $v$  in the exchange term. This modification makes no difference in the ion plus outer electron case since there the exchange term anyhow is small. For an electron gas on the other hand it is the second term rather than the first which is important. The first term is local in space and thus by translational invariance it is a constant and gives only a constant shift of the quasi-particle energies. The second term is similar to the one used by Pines <sup>36)</sup> to evaluate single-particle properties, though the screening lengths are somewhat different. Thus e.g. the anomaly for the specific heat of an electron gas which appears in a HF approximation, is not present when a screened potential is used, as shown already by Wohlfarth <sup>9)</sup>.

Although the first term is trivial for an electron gas it may be quite important for a real solid. This term has been considered by Callaway <sup>8)</sup> for alkali metals. Unfortunately for this discussion he only estimates its effect on the cohesive energy rather than on the band structure. Phillips <sup>27)</sup> argues from a different type of approach that this term should have little importance in the weakly periodic case. It should, however, be realized that even though this term might be essentially constant within a band it could differ appreciably between bands. Another type of approach using a "projected wave field" has recently been made by Bassani, Robinson, Goodman and Schrieffer <sup>37)</sup>. This approach is adepted to utilize the rapid convergence of the "Orthogonalized Plane Wave" method. The basic physical idea is that the core electrons can be treated dynamically independent of the valence electrons.

If we should like to calculate  $M^{(1)}$  through the linear response function and want to keep the approximation (39), we have to take it in the static limit, that is  $\epsilon = 0$ . The complete expression for the real part of  $V_p$  is given by (B24). It involves the real part of the response function as well as the imaginary part which is a kind of oscillator strength,  $R^{(2)}(\omega)$  gives a measure of the probability for a transition between the ground state

The main advantage of the Green function formalism as compared with a simple physical description by a many-electron wave function is its close connection with simple physical ideas. Thus we are able to use the classical concept of a particle, or quasi-particle, having an energy and a life time, in a further expect that a moderate error in the self energy operator  $M$  gives a description which has an exact meaning also in a many-body system. We may further expect that a many-body problem is so large and since the mathematical complexity of the equation schemes. It is felt that since the mathematical complexity of the equation of motion is more unbalanced in the case where two macroscopically large total excitation energies are subtracted to yield an excitation energy.

To proceed beyond the general formulation we need good approximations. It should be observed that there are many mathematical problems, so far unsolved, connected with the  $M$ -operator. When we consider the spectrum of the equation with the energy-dependent  $M$ -operator we find that the energy eigenvalues range from  $-\infty$  to  $+\infty$ . Some of these exact orbitals have no counterpart in  $G(0)$  and they probably have little relevance to single-particle behavior. If it in future applications should turn out to be possible to aim at so high an accuracy that these orbitals acquire importance it is probably better to work with the equation for  $G$  rather than with the equation for the amplitudes. In most applications, however, we have to be content with using a fixed energy value in the  $M$ -operator and to take the hermitian part in case of a continuous spectrum. The energy spectrum then has a finite lower limit and the solution that is wanted can be picked out as say the one corresponding to the third lowest eigenvalue after symmetry separation.

## CONCLUDING REMARKS

and an excited state having an energy  $\omega$  above the ground state. If necessary a spin-orbit term of the usual structure can simply be added to the  $M$ -operator. Also the spin-orbit term should really contain some polarization (G. W. Pratt, private communication).

has been carried out.

Also in the present context we are faced with a self-consistency problem. When a specific type of approximation for the M-operator is chosen we have to iterate to obtain self-consistently the orbitals which form the propagator  $G$ . In a specific step of this procedure, solving for the orbitals using a rough potential, we may of course utilize the variational principle. We may also convert this intermediate problem to matrix form, expanding the orbitals in a fixed truncated basis set of say  $r$  functions. The  $r$  orbital solutions we then obtain provide the corresponding truncation of the infinite summation appearing in  $v_p^{(1)}$ , eq. (B24).

The present formalism is so far inadequate in treating multiplicity splittings. The main applicability is to atoms, molecules and solids with one electron outside a closed configuration and to metals where there are so many electrons outside a closed configuration (the ions) that coupling between spins of different conduction electrons become unimportant.

The instability sometimes observed in calculating orbital energies in the HF method could very well be related to this failure of taking multiplicity splittings into account. The density matrix is, however, quite stable and that is all that is needed as regards the excited orbitals. Specifically as regards band structure the exact theory makes predictions only for excitations close to the Fermi surface and there is hence an additional reason to regard the lower bands as less significant.

It should finally be recognized that the development given in the last few sections of one-electron behaviour is by no means complete. Thus e.g. the vibrations of the atoms can very well give an influence on the quasi-particle spectrum comparable to the polarization effects <sup>38)</sup>. Further in considering transport processes not only the quasi-particle spectrum is important but also the effective field inside the solid, the calculation of which is quite a problem in itself. Transport processes are perhaps most effectively treated with the temperature dependent Green function formalism.

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APPENDIX

A. APPROXIMATION OF THE M OPERATOR  
THROUGH AN ITERATION PROCEDURE

The equation of motion for the field operator in the Heisenberg representation is

$$i \frac{\partial}{\partial t} \psi(x) = [\psi(x), H] . \quad (A1)$$

After evaluating the commutator we have

$$\left( i \frac{\partial}{\partial t} - h(x) - \int v(x, x') f(x') dx' \right) \psi(x) = 0, \quad (A2)$$

where

$$\begin{aligned} f(x) &= \psi^+(x) \psi(x), \quad \psi(x) = e^{iHt} \psi(x) e^{-iHt}, \quad \psi(x) = \sum_k a_k u_k(x) \\ H &= \int \psi^+(x) h(x) \psi(x) dx + \frac{1}{2} \int \psi^+(x) \psi^+(x') v(x, x') \psi(x') \psi(x) dx dx' \end{aligned} \quad (A3)$$

The functions  $u_k$  form a complete orthonormal set and  $a_k$  is an annihilation operator. An equation for the Green function is now easily obtained from (A2),

$$\left( i \frac{\partial}{\partial t} - h(1) \right) G(1, 1') + i \int v(1', 2) G(2, 1, 2', 1') \delta(2) = \delta(1, 1'), \quad (A4)$$

where

$$\begin{aligned} G(1, 2) &= (-i) \langle T(\psi(1) \psi^+(2)) \rangle \\ G(1, 2; 1', 2') &= (-i)^2 \langle T(\psi(1) \psi(2) \psi^+(2') \psi^+(1')) \rangle \\ (1') &= (x_1, t_1 + \Delta), \quad \Delta > 0 \text{ and infinitesimal.} \end{aligned} \quad (A5)$$

In eq. (A4) the first and second order Green functions are coupled. Martin and Schwinger<sup>23)</sup> have shown that the term with  $G(1, 2; 1', 2')$  can be expressed as a functional derivative of  $G(1, 2)$ . Since their proof is rather complicated and not very explicit we will rederive the functional derivative expression by elementary methods.

Consider a Hamiltonian  $H_s$  in the Schrödinger picture

$$H_s = H_s^{(e)} + w_s(t) \quad (A6)$$

where  $H_s^{(0)}$  is identical with the Hamiltonian  $H$  defined in (A3) and  $w_s(t)$  is a small perturbing time dependent potential

$$w_s(t) = \int p(\underline{x}) w(\underline{x}, t) d\underline{x}, \quad p(\underline{x}) = \psi^*(\underline{x}) \psi(\underline{x}) \quad (A7)$$

where  $w(\underline{x}, t)$  is taken as spin independent ( $\underline{x}$  involves in general both space and spin). The time evolution of the state vector in the Schrödinger picture is described by an operator  $V(t, t')$ ,

$$|t\rangle_s = V(t, t') |t'\rangle_s. \quad (A8)$$

Since  $|t\rangle_s$  satisfies the Schrödinger equation,  $V(t, t')$  has to satisfy

$$i \frac{d}{dt} V(t, t') = (H_s^{(e)} + w_s(t)) V(t, t'); \quad V(t, t) = 1. \quad (A9)$$

We also introduce the unperturbed time evolution operator  $U(t, t') = e^{-iH(t-t')}$ , which satisfies

$$i \frac{d}{dt} U(t, t') = H_s^{(e)} U(t, t'); \quad U(t, t) = 1. \quad (A10)$$

The differential eq. (A9) is then converted into an integral eq.

$$V(t, t') = U(t, t') - i \int_{t'}^t U(t, t'') w_s(t'') V(t'', t') dt''. \quad (A11)$$

The crucial quantity we need is the functional derivative of  $V(t, t')$  with respect to the perturbing potential  $w(\underline{x}, t)$ , which from (A11) becomes,

$$\begin{aligned} \frac{\delta V(t, t')}{\delta w(t_2)} &= \frac{\delta V(t, t')}{\delta w(\underline{x}_2, t_2)} = \\ &= -i \operatorname{sgn}(t-t') U(t, t_2) p(\underline{x}_2) V(t_2, t') - i \int_{t'}^t U(t, t'') w_s(t'') \frac{\delta V(t'', t')}{\delta w(t_2)} dt'' \quad (A12) \end{aligned}$$

$$\operatorname{sgn} t = \begin{cases} +1 & t > 0 \\ -1 & t < 0 \end{cases}$$

when  $t_2$  is in the time interval determined by  $t$  and  $t'$ , otherwise  $\frac{\delta V}{\delta w}$  is zero. Putting  $w = 0$  in (A12) we have

$$\left[ \frac{\delta V(t, t')}{\delta w(t_2)} \right]_{w=0} = -i \operatorname{sgn}(t-t') U(t, t_2) p(\underline{x}_2) U(t_2, t'). \quad (A13)$$

The general expression for the functional derivative in question is

$$\frac{\delta V(t, t')}{\delta w(t_2)} = -i \operatorname{sgn}(t-t') V(t, t_2) p(\underline{x}_2) V(t_2, t'), \quad (A14)$$

as can be verified by substituting (A14) into (A12).

It is convenient to introduce the following type of expectation values to use in the Green functions

$$\langle \psi(x) \psi^*(x') \rangle = \frac{\langle t_0 | U(t_0, T) V(T, t_0) \psi_H(x) \psi_H^*(x') | t_0 \rangle_s}{\langle t_0 | U(t_0, T) V(T, t_0) | t_0 \rangle_s} \quad (A15)$$

where  $\psi_H(x) = V(t_0, t) \psi(x) V(t, t_0)$ . We consider  $t_0$  to be some time in the distant past and  $|t_0\rangle_s$  to be the ground state of  $H$ .  $T$  is a time far in the future and we do not allow  $w(t)$  to be different from zero for other  $t$  than those in the interval between  $t_0$  and  $T$ . When  $w(t)$  is zero for all  $t$  the definition (A15) gives the expectation value of Heisenberg operators with respect to the ground state, cf eq. (5). The matrix element in (A15) has the same structure as those used in scattering theory, that is a matrix element between unperturbed states at times far in the future,  $U(T, t_0)|t_0\rangle_s$ , and far in the past,  $|t_0\rangle_s$ , with a scattering matrix  $V(T, t_0)$  inserted.

With the present definition of matrix elements the equation for  $G(1, 1')$  becomes

$$(i \frac{\partial}{\partial t} - h(x) - w(x, t)) G(1, 1') + i \int v(1^+, 2) G(2, 1; 2^+, 1') = \delta(1, 1') \quad (A16)$$

The term containing the second order Green function can be rewritten by aid of the equation

$$\begin{aligned} \frac{\delta G(1, 1')}{\delta w(2)} &= - \langle T(\rho(2) \psi(1) \psi^*(1')) \rangle + i G(1, 1') \langle \rho(2) \rangle = \\ &= - G(2, 1; 2^+, 1') + i G(1, 1') \langle \rho(2) \rangle. \end{aligned} \quad (A17)$$

Thus equation (A16) becomes

$$(i \frac{\partial}{\partial t} - h(1) - V(1)) G(1, 1') - i \int v(1^+, 2) \frac{\delta G(1, 1')}{\delta w(2)} \lambda(2) = \delta(1, 1') \quad (A18)$$

where

$$V(1) = w(1) + \int v(1, 2) \langle \rho(2) \rangle \lambda(2). \quad (A19)$$

To obtain an iteration procedure for solving (A18), it is essential to introduce the inverse of the Green function,

$$\int G^{-1}(1, 2) G(2, 1') \lambda(2) = \delta(1, 1'). \quad (A20)$$

We further note that

$$\frac{\delta G(1, 1')}{\delta w(3)} = -i \int G(1, 2') \frac{\delta G^{-1}(2', 2)}{\delta w(3)} G(2, 1') \lambda(2) \lambda(2'). \quad (A21)$$

We choose to define the zero order Green function by the Hartree-like equation,

$$\left( i \frac{\partial}{\partial t} - h(1) - V(1) \right) G^{(0)}(1,1') = \delta(1,1') , \quad (A22)$$

and hence the self energy operator  $M$  becomes

$$M(1,2) = -i \int v(1',3) G(1,2') \frac{\delta G^{(0)}(2',2)}{\delta v(3)} \Delta(2') \Delta(3) , \quad (A23)$$

since (A23) inserted in (A18) gives

$$\left( i \frac{\partial}{\partial t} - h(1) - V(1) \right) G(1,1') - \int M(1,2) G(2,1') \Delta(2) = \delta(1,1') . \quad (A24)$$

With a specific approximation for  $M$ , the corresponding approximation for  $G$  can be obtained from eq. (A24) and put back into eq. (A23), thus giving the next iteration step in the approximation sequence for  $M$ . The first approximation for  $M$  is obtained by using  $G^{(0)}$  in eq. (A23),

$$\begin{aligned} M^{(1)}(1,2) &= -i \int v(1',3) G^{(0)}(1,2') \frac{\delta}{\delta v(3)} G^{(0)}(2',2) \Delta(2') \Delta(3) = \\ &= -i \int G^{(0)}(1,2') \mathcal{V}(1,4) \frac{\delta}{\delta v(4)} G^{(0)}(2',2) \Delta(2') \Delta(4) = \\ &= i G^{(0)}(1,2) \mathcal{V}(1,2) \end{aligned} \quad (A25)$$

Here the Hubbard effective potential  $\mathcal{V}$  has been introduced,

$$\begin{aligned} \mathcal{V}(1,2) &= \int v(1',3) \frac{\delta}{\delta v(3)} V(2) \Delta(3) = \\ &= v(1',2) - i \int v(1',3) \langle T(\rho(3) \rho(4)) \rangle v(4,2) \Delta(3) \Delta(4) . \end{aligned} \quad (A26)$$

The next approximation for  $M$  is obtained by calculating  $G^{(1)}$  from the equation

$$\left( i \frac{\partial}{\partial t} - h(1) - V(1) \right) G^{(1)}(1,1') - \int M^{(1)}(1,2) G^{(1)}(2,1') \Delta(2) = \delta(1,1') , \quad (A27)$$

and then use the solution in (A23),

$$\begin{aligned} M^{(2)}(1,2) &= -i \int v(1',3) G^{(1)}(1,2') \frac{\delta}{\delta v(3)} G^{(1)}(2',2) \Delta(2') \Delta(3) = \\ &= i G^{(1)}(1,2) \mathcal{V}(1,2) + i \int v(1',3) G^{(1)}(1,2') \frac{\delta}{\delta v(3)} M^{(1)}(2',2) \Delta(2') \Delta(3) . \end{aligned} \quad (A28)$$

To calculate the functional derivative of  $M^{(1)}$  we need those of  $G^{(0)}$  and  $\mathcal{V}$ .

$$\begin{aligned} \frac{\delta G^{(0)}(2', 2)}{\delta w(3)} &= - \int \frac{\delta V(4)}{\delta w(3)} G^{(0)}(2', 5) \frac{\delta G^{(0)}(5, 6)}{\delta V(4)} G^{(0)}(6, 2) \delta(4) \delta(5) \delta(6) = \\ &= \int \frac{\delta V(4)}{\delta w(3)} G^{(0)}(2', 4) G^{(0)}(4, 2) \delta(4) \end{aligned} \quad (A29)$$

$$\frac{\delta \mathcal{V}(2', 2)}{\delta w(3)} = - \int V(2', 4) V(2, 5) \langle T(\rho'(3) \rho'(4) \rho'(5)) \rangle \delta(4) \delta(5) .$$

The expression for  $M^{(2)}$  becomes,

$$\begin{aligned} M^{(2)}(1, 2) &= i G^{(0)}(1, 2) \mathcal{V}(1, 2) - \int \mathcal{V}(1, 4) G^{(0)}(2', 4) G^{(1)}(4, 2) \mathcal{V}(2', 2) \delta(2) \delta(4) + \\ &+ \int \langle T(\rho'(3) \rho'(4) \rho'(5)) \rangle V(1, 3) V(2', 4) V(2, 5) G^{(1)}(1, 2') G^{(0)}(2', 2) \delta(3) \delta(4) \delta(5). \end{aligned} \quad (A30)$$

If we use the symbols

$$\begin{array}{ccc} \overrightarrow{1} & \text{wavy line} & \text{dashed line} \\ G(1, 2) & \mathcal{V}(1, 2) & V(1, 2) \end{array} \quad (A31)$$

the approximation we have now obtained for  $V+M$  can be written (we neglect the difference between  $G^{(0)}$  and  $G^{(1)}$ , and represent them with the symbol for  $G$ ),

$$\begin{array}{c} \text{dashed circle} \\ + \end{array} \quad \begin{array}{c} \text{wavy line} \\ \text{dashed line} \end{array} \quad + \quad \begin{array}{c} \text{dashed circle} \\ \text{wavy line} \end{array} \quad + \quad \begin{array}{c} \text{dashed circle} \\ \text{dashed line} \end{array} \quad (A32)$$

where  $\rho^{(3)}$  stands for the three particle correlation function in eq. (A30). The first term in  $M^{(1)}$  and  $M^{(2)}$  obviously converges to  $iG(1, 2) \mathcal{V}(1, 2)$ , and we have not always been careful to state what kind of approximation for  $G$  is considered. The perturbing potential  $w$  is of course to be put equal to zero once the expression for the required approximation has been obtained.

B. THE SPECTRAL RESOLUTION OF  $M^{(1)}$  AND ITS  
RELATION TO THE LINEAR RESPONSE FUNCTION

We Fourier transform eq. (A24) with respect to the time difference,  $t-t' = \tau$ ,

$$(e - h(1) - V(1))G(1, t'; e) - \int M(1, 2; e)G(2, t'; e) d(x_2) = \delta(x_1, x_1'). \quad (B1)$$

For the  $M$  operator we take the approximation (A25)

$$M^{(1)}(1, 2; e) = i \int_{-\infty}^{\infty} G(1, 2; \tau) V(1, 2; \tau) e^{i\epsilon\tau} d\tau = \frac{i}{2\pi} \int_{-\infty}^{\infty} G(1, 2; e - e') V(1, 2; e') de' \quad (B2)$$

The  $v(1^+, 2)$  term in  $\mathcal{V}(1, 2)$ , eq. (A26) gives a HF type exchange term,

$$\begin{aligned} i \int_{-\infty}^{\infty} G(1, 2; \tau) v(x_1, x_2) \delta(\tau + \Delta) e^{i\epsilon\tau} d\tau &= i v(x_1, x_2) G(x_1, x_2; -\Delta) = \\ &= -v(x_1, x_2) \rho(x_1, x_2). \end{aligned} \quad (B3)$$

For the remaining part of the  $M^{(1)}$  operator we introduce the name polarization potential,  $V_p(1, 2; e)$ .

$$M^{(1)}(1, 2; e) = -v(x_1, x_2) \rho(x_1, x_2) + V_p(x_1, x_2; e). \quad (B4)$$

The spectral resolution of  $G$  has already been given, eq. (10). We rewrite it in a slightly more compact form

$$G(x_1, x_2; e) = \sum_m \frac{\varphi_m(x_1) \varphi_m^*(x_2)}{e - \epsilon_m}, \quad (B5)$$

where  $\varphi_m$  stands for both the  $f_k$  and the  $g_l$  and  $\epsilon_m$  is either  $\epsilon_k - i\Delta$  or  $\epsilon_l + i\Delta$ . Since  $\epsilon_k > \mu > \epsilon_l$  the poles of  $G(1, 2; e)$  are distributed according to figure 2.

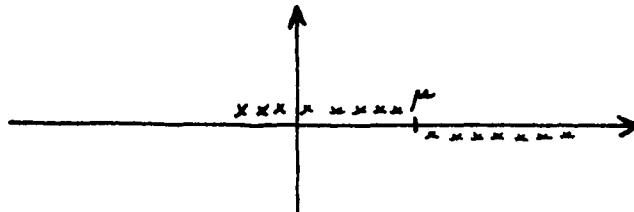


Figure 2.

Note that  $\mu$  is somewhat arbitrary for a discrete spectrum and could there be taken as e.g. the mean value of the smallest  $\epsilon_k$  and the largest  $\epsilon_l$ . We also make a spectral resolution of the part of  $\mathcal{V}$  that remains after  $v$  is taken away,

$$\begin{aligned}
 & \int_{-\infty}^{\infty} e^{i\epsilon(t_1-t_2)} \delta_{t_1}(-i) \int \mathcal{V}(1,3) \langle T(\rho'(3)\rho'(4)) \rangle \mathcal{V}(4,2) \delta(3) \delta(4) = \\
 & = \int_{-\infty}^{\infty} e^{i\epsilon\tau} \delta_{\tau}(-i) \int \mathcal{V}(x_1, x_3) \mathcal{V}(x_2, x_4) \delta x_3 \delta x_4 \left[ \langle \rho(x_3) e^{-i(H-E_0)\tau} \rho(x_4) \rangle \Theta(\tau) + \right. \\
 & \quad \left. + \langle \rho(x_4) e^{i(H-E_0)\tau} \rho(x_3) \rangle \Theta(-\tau) - \langle \rho(x_3) \rangle \langle \rho(x_4) \rangle \right] = \\
 & = \sum'_{s} \frac{P_s(x_1) P_s^*(x_2)}{\epsilon - \epsilon_s + i\Delta} - \sum'_{s} \frac{P_s^*(x_1) P_s(x_2)}{\epsilon + \epsilon_s - i\Delta} = F(1,2;\epsilon) + F(1,2;-\epsilon). \quad (B6) \\
 F(1,2;\epsilon) & = \sum'_{s} \frac{P_s(x_1) P_s^*(x_2)}{\epsilon - \epsilon_s + i\Delta}, \quad \begin{cases} P_s(x) = \int \mathcal{V}(x, x') \langle N | \rho(x') | N, s \rangle \\ \epsilon_s = E_{N,s} - E_N \end{cases}
 \end{aligned}$$

The prime on the sums stands for deleting the term with  $s = 0$ . In writing the last step of (B6) we have used the fact that  $\sum_{s, \epsilon_s = \text{const}} P_s(x) P_s^*(x')$  is real, which is true also when we use complex wave functions. Thus we have for the polarization potential  $V_p$ ,

$$V_p(1,2;\epsilon) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \sum_m \frac{\phi_m(1) \phi_m^*(2)}{\epsilon - \epsilon' - \epsilon_m} (F(1,2;\epsilon') + F(1,2;-\epsilon')) d\epsilon'. \quad (B7)$$

We first consider the evaluation of a typical term of the contribution from  $F(1,2;\epsilon')$ ,

$$\int_{-\infty}^{\infty} \frac{1}{\epsilon - \epsilon' - \epsilon_m} \frac{1}{\epsilon' - \epsilon_s + i\Delta} d\epsilon'. \quad (B8)$$

We can close the contour by a large semi circle in either the upper or the lower half plane since the integral tends to zero as fast as  $(\epsilon')^{-2}$ . We choose the upper half plane in this case and thus we have a contribution only when  $\epsilon_m$  corresponds to a particle,  $\epsilon_m = \epsilon_k$ ,

$$(-2\pi i) \frac{1}{\epsilon - \epsilon_m - \epsilon_s + i\Delta} \Theta(\epsilon_m - \mu) \quad (B9)$$

The imaginary part of  $\epsilon_m$  can now be absorbed in  $i\Delta$  and we consider  $\epsilon_m$  to be real henceforth. The contribution from  $F(1,2;-\epsilon')$  is obtained similarly by closing the contour in the lower half plane. The complete expression for  $V_p$  becomes,

$$\begin{aligned}
 V_p(1,2;\epsilon) & = \sum_m \sum'_{s} \phi_m(1) \phi_m^*(2) P_s(1) P_s^*(2) \left( \frac{\Theta(\epsilon_m - \mu)}{\epsilon - \epsilon_m - \epsilon_s + i\Delta} - \frac{\Theta(\mu - \epsilon_m)}{\epsilon_m - \epsilon_s - \epsilon + i\Delta} \right) = \\
 & = \sum_m \phi_m(1) \phi_m^*(2) [F(1,2;\epsilon - \epsilon_m) \Theta(\epsilon_m - \mu) - F(1,2;\epsilon_m - \epsilon) \Theta(\mu - \epsilon_m)]. \quad (B10)
 \end{aligned}$$

We now want to relate the polarization potential  $V_p$  to the linear response function  $R$ . To obtain  $R$  we consider a small external charge density,  $\rho_{ex}(\underline{x}, t)$ , and calculate in a linear approximation the induced charge density  $\rho_{ind}(\underline{x}, t)$ . This induced charge density gives rise to an induced potential  $\phi(\underline{x}, t)$ . We define  $R$  by the relation

$$\phi(\underline{x}, t) = \frac{1}{2} \int \mathcal{V}(\underline{x}, \underline{x}') \rho_{ind}(\underline{x}', t) d\underline{x}' = \int_{-\infty}^t dt' \int d\underline{x}' R(\underline{x}, \underline{x}'; t-t') \rho_{ext}(\underline{x}', t'). \quad (B11)$$

The induced charge density,  $\rho_{ind}$ , from a perturbing potential  $w$ , is according to (A8) and (A11), in the linear approximation,

$$\begin{aligned} \rho_{ind}(\underline{x}, t) &= \langle t_0 | V(t_0, t) \rho(\underline{x}) V(t, t_0) | t_0 \rangle - \langle t_0 | U(t_0, t) \rho(\underline{x}) U(t, t_0) | t_0 \rangle = \\ &= i \int_{t_0}^t \langle t_0 | [w_H(t'), \rho_H(\underline{x}, t)] | t_0 \rangle dt'. \end{aligned} \quad (B12)$$

We take, cf eq. (A7),

$$w_s(t) = \int \rho(\underline{x}') \mathcal{V}(\underline{x}', \underline{x}'') \rho_{ext}(\underline{x}'', t) d\underline{x}' d\underline{x}''. \quad (B13)$$

From (B12) we then have, putting  $t_0 = -\infty$ ,

$$\rho_{ind}(\underline{x}, t) = i \int_{-\infty}^t dt' \int d\underline{x}' d\underline{x}'' \langle t_0 | [ \rho(\underline{x}', t'), \rho(\underline{x}, t) ] | t_0 \rangle \mathcal{V}(\underline{x}', \underline{x}'') \rho_{ext}(\underline{x}'', t'), \quad (B14)$$

and comparing with (B11) we obtain

$$R(1,2; t, -t) = -\frac{i}{2} \int \langle t_0 | [ \rho(1'), \rho(2') ] | t_0 \rangle \mathcal{V}(1,1') \mathcal{V}(2,2') d(1') d(2'). \quad (B15)$$

When we compare  $R$  with the polarization part of  $\mathcal{V}$ , eq. (A26), we find that the main difference is that  $R$  has a commutator instead of a time-ordering operator. The Fourier transform of  $R$  with respect to time is,

$$R(1,2; \epsilon) = \int_0^\infty R(1,2; \tau) e^{i\epsilon\tau} d\tau = \frac{1}{2} (F(1,2; \epsilon) + F^*(1,2; -\epsilon)). \quad (B16)$$

The reason that we have taken 0 to  $\infty$  as integration limits rather than  $-\infty$  to  $\infty$ , is that  $R(1,2; \tau)$  does not appear for  $\tau < 0$  in eq. (B11). We now relate the imaginary part of  $V_p$  to  $R$ . From the definition of  $F$  we have that,

$$\text{Im } F(1,2; \epsilon) \equiv F^{(2)}(1,2; \epsilon) = 0 \quad \text{for } \epsilon < 0, \quad (B17)$$

and thus from (B10) and (B16),

$$\operatorname{Im} V_p(1,2;\epsilon) \equiv V_p^{(2)}(1,2;\epsilon) = 2 \sum_m \rho_m(1) \rho_m^*(2) R^{(1)}(1,2;\epsilon - \epsilon_m) [\theta(\epsilon - \epsilon_m) \theta(\epsilon_m - \mu) + \theta(\mu - \epsilon_m) \theta(\epsilon_m - \epsilon)], \quad (B18)$$

where we have used the relations,

$$\begin{aligned} F^{(1)}(1,2;\epsilon) &= 2 R^{(2)}(1,2;\epsilon) \quad \text{for } \epsilon > 0 \\ R^{(2)}(1,2;\epsilon) &= - R^{(2)}(1,2;-\epsilon) . \end{aligned} \quad (B19)$$

From (B18) we find immediately,

$$V_p^{(2)}(1,2;\mu) = 0 , \quad (B20)$$

which relation has to be satisfied from general considerations, as shown by Luttinger. We next want to relate the real part of  $V_p$  to  $R$ , and to that end we write,

$$F^{(1)}(1,2;\epsilon) = R^{(1)}(1,2;\epsilon) + \frac{1}{2} (F^{(1)}(1,2;\epsilon) - F^{(1)}(1,2;-\epsilon)) . \quad (B21)$$

The second term of (B21) can be expressed in  $R^{(2)}$ . Since

$$R^{(1)}(1,2;\epsilon) = \frac{\pi}{2} \sum_s' P_s(1) P_s^*(2) (\delta(\epsilon + \epsilon_s) - \delta(\epsilon - \epsilon_s)) , \quad (B22)$$

we have

$$\frac{1}{2} (F^{(1)}(1,2;\epsilon) - F^{(1)}(1,2;-\epsilon)) = \sum_s' P_s(1) P_s^*(2) \frac{\epsilon}{\epsilon^2 - \epsilon_s^2} = -\frac{\pi}{\pi} \int_0^\infty \frac{\epsilon}{\epsilon^2 - \omega^2} R^{(2)}(1,2;\omega) d\omega . \quad (B23)$$

From (B10), (B21), and (B23) we finally have,

$$\begin{aligned} V_p^{(1)}(1,2;\epsilon) &= \sum_m \rho_m(1) \rho_m^*(2) \left[ R^{(1)}(1,2;\epsilon - \epsilon_m) \theta(\epsilon_m - \mu) - R^{(1)}(1,2;\epsilon_m - \epsilon) \theta(\mu - \epsilon_m) - \right. \\ &\quad \left. - \frac{\pi}{\pi} \int_0^\infty \frac{\epsilon - \epsilon_m}{(\epsilon - \epsilon_m)^2 - \omega^2} R^{(2)}(1,2;\omega) d\omega \right] . \end{aligned} \quad (B24)$$

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